



## PATENT SPECIFICATION

NO DRAWINGS

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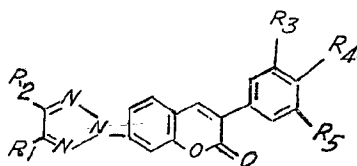
## COMPLETE SPECIFICATION

## 7-v-Triazolyl-(2)-Coumarin Compounds

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention comprises new and valuable 7 - v - triazolyl - (2) - coumarin compounds, the production thereof, and the use thereof as brightening agents.

The new compounds are blue-fluorescent 7 - v - triazolyl - (2) - coumarin compounds of the formula:



(I)

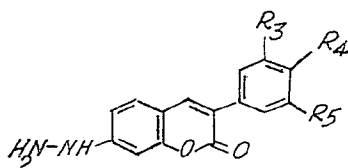
wherein  $R_1$  is hydrogen or an unsubstituted or substituted alkyl or aryl radical,  $R_2$  is an unsubstituted or substituted alkyl or aryl radical, cyano, a carboxylic acid group, a carboxylic acid ester group, an unsubstituted or substituted carboxylic acid amide group or an acylated amino group, and  $R_3$ ,  $R_4$  and  $R_5$  independently of one another, stand for hydrogen, halogen, alkyl radicals or alkoxy groups.

The new compounds are suitable for

brightening a great variety of materials such as fibres, filaments, fabrics, knitted fabrics and foils of synthetic origin, and especially for brightening materials made of polyesters or polyvinyl chloride and for brightening lacquers and varnishes of cellulose esters or nitrocellulose. The compounds can be applied as brightening agents in the usual manner, for example, in the form of aqueous dispersions or in the form of solutions in inert solvents; if desired, they can also be applied in combination with detergents or they can be added to casting masses serving for the production of foils or filaments or other shaped articles. The amounts of the 7 - v - triazolyl - (2) - coumarin compounds of the formula (I) required for brightening purposes can easily be established by preliminary experiments; in general, amounts of 0.1 to 1% of the compounds referred to the weight of the material to be treated will be sufficient. The brightening effects obtained by means of the 7 - v - triazolyl - (2) - coumarin compounds of the formula (I) are very fast to light and have an excellent fastness to washing. The coumarin compounds hitherto proposed as brightening agents do not have these valuable properties to the same extent.

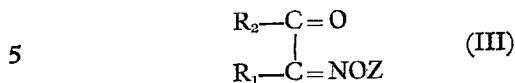
The 7 - v - triazolyl - (2) - coumarin compounds of the present invention can be prepared by various methods. Those compounds which correspond to the formula (I) wherein  $R_2$  stands for an optionally substituted alkyl or aryl radical, while the symbols  $R_1$ ,  $R_3$ ,  $R_4$  and  $R_5$  have the same meaning as above, can be obtained, for example, by condensing

7-hydrazino-coumarin derivatives of the formula

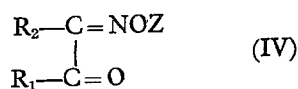


(II)

with  $\alpha$ -oximino-ketones of the formulae



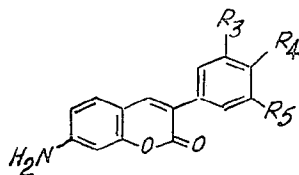
or



10 wherein Z stands for hydrogen or an acyl radical, for example, an acetyl radical, and converting the resultant  $\alpha$ -oximinohydrazones into the 7 - v - triazolyl - (2) - coumarin compounds with the elimination of HOZ.

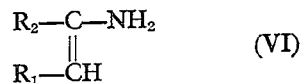
15 7 - v - Triazolyl - (2) - coumarin compounds of the formula (I) wherein  $R_2$  stands for cyano, a carboxyl group, a carboxylic acid ester group or an optionally substituted carboxylic acid amide group, while the symbols  $R_1$ ,  $R_3$ ,  $R_4$  and  $R_5$  have the same meaning as above, can be obtained, for example, by

20 coupling diazo compounds of 7-amino-coumarin derivatives of the formula



(V)

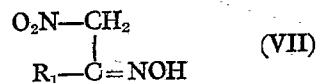
with enamines of the formula



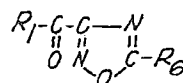
25 for example, with  $\beta$ -amino-crotonic acid nitrile,  $\beta$ -amino-crotonic acid esters or amides or with  $\beta$ -amino-cinnamic acid nitrile,  $\beta$ -amino-cinnamic acid esters or amides, converting the resultant azo compounds with an ammoniacal solution of a copper (II) salt into the copper complexes, transforming the latter into the 7 - v - triazolyl - (2) - coumarin compounds by heating and, if desired, hydrolysing the carboxylic acid nitrile, ester or amide group

35 to form the carboxyl group.

7 - v - Triazolyl - (2) - coumarin compounds of the formula (I) wherein  $R_2$  stands for an acylated amino group, while  $R_1$ ,  $R_3$ ,  $R_4$ , and  $R_5$  have the same meaning as above, can be obtained, for example, by coupling diazo compounds of 7-amino-coumarin derivatives of the formula (V) with  $\alpha$ -nitro-oximes of the formula

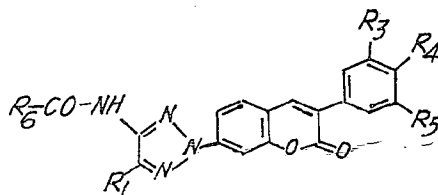


for example, with nitro-acetaldoxime or with  $\omega$  - nitro - acetophenone - oxime, cyclising the resultant azo compounds to form the corresponding 7 - [4 - nitro - triazolyl - (2)] - coumarin compounds, reducing the nitro group to the amino group and converting the latter into the acylamino group  $R_6$ . 7 - v - Triazolyl - (2) - coumarin compounds of the formula (I) wherein  $R_2$  stands for an acylated amino group and  $R_1$  stands for an optionally substituted aryl radical, while  $R_3$ ,  $R_4$  and  $R_5$  have the same meaning as above, can also be obtained by condensing 7 - hydrazino - coumarin compounds of the formula (II) with 1,2,4-oxodiazoles of the formula



(VIII)

wherein  $R_6$  stands for an alkyl or aryl radical, rearranging the resultant hydrazones to form 7 - v - triazolyl - (2) - coumarin compounds of the formula



(IX)

and, if necessary, replacing the acylamino group  $R_6-CO-NH$  with the acylamino group  $R_2$ .

The following Examples serve to illustrate the invention:—

#### EXAMPLE 1

A fabric of polyester fibres is padded with an aqueous liquor containing, per litre, 1 g of one of the 7 - v - triazolyl - (2) - coumarin

compounds of formula (I) listed in the Table below under (a)–(q) as brightening agent and 3 g of a commercial dispersing agent based on fatty alcohol polyglycol ethers. The fabric is  
5 squeezed to a weight increase of 100%, then

dried and heated at 120° C for 30 minutes. Compared with untreated material, the fabric thus treated exhibits a strong neutral brightening effect of good fastness to light.

7-v-Triazolyl-(2)-coumarin compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Melting point °C
(a)	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	232–234°
(b)	H	C <sub>6</sub> H <sub>5</sub>	H	H	H	246°
(c)	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	H	H	161–162°
(d)	CH <sub>3</sub>	p-Cl-C <sub>6</sub> H <sub>4</sub>	H	H	H	189–192°
(e)	CH <sub>3</sub>	o-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	H	H	H	180–181°
(f)	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	H	232°
(g)	H	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	H	247°
(h)	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	H	192–193°
(i)	CH <sub>3</sub>	p-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	H	CH <sub>3</sub>	H	232–234°
(k)	CH <sub>3</sub>	p-Cl-C <sub>6</sub> H <sub>4</sub>	H	CH <sub>3</sub>	H	245–246°
(l)	CH <sub>3</sub>	o-Cl-C <sub>6</sub> H <sub>4</sub>	H	CH <sub>3</sub>	H	210–212°
(m)	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	H	228–229°
(n)	C <sub>6</sub> H <sub>5</sub>	CONH <sub>2</sub>	H	H	H	264–265°
(o)	CH <sub>3</sub>	COOC <sub>2</sub> H <sub>5</sub>	H	H	H	202–203°
(p)	C <sub>6</sub> H <sub>5</sub>	CONH <sub>2</sub>	H	CH <sub>3</sub>	H	286–287°
(q)	CH <sub>3</sub>	COOC <sub>2</sub> H <sub>5</sub>	H	CH <sub>3</sub>	H	204–206°

The compound listed in the Table under (a) was prepared in the following manner:

- 25.2 Grams (0.1 mole) 3 - phenyl - 7 - hydrazino - coumarin were heated with 12.0 g (0.12 mole) diacetyl monoxime and 10 ml of a 50% acetic acid in 400 ml ethanol solution while stirring and cooling under reflux. When free hydrazine was no longer indicated in a spot test with o-naphthoquinone-sulphonic acid, as was the case after about one hour, the mixture was cooled and the precipitated yellow condensation product filtered off with suction. 30 Grams of the  $\alpha$ -oximino-hydrazone so obtained were then heated under reflux with 400 ml acetic anhydride, 20 g of anhydrous sodium acetate and 20 ml acetic acid for 8 hours. The acetic acid and part of the excess acetic anhydride were subsequently distilled off under reduced pressure. The precipitated pale yellow brightening agent was filtered off with suc-

tion, washed with cold methanol and dried.

The 7 - v - triazolyl - (2) - coumarin compounds listed under (b) to (m) were prepared in an analogous manner. For the preparation of the compounds listed under (b), (c), (d) and (e) as well as under (g) to (m) the diacetyl monoxime used for the preparation of the compounds listed under (a) and (f) was replaced with oximino-acetophenone (b;g), oximino - propiophenone or 1 - oximino - 1 - phenylacetone (c;h), 1 - oximino - 1 - p - chlorophenyl - acetone (d;k), 1 - oximino - 1 - o - tolyl - acetone (e), 1 - oximino - 1 - p - tolyl - acetone (i), 1 - oximino - 1 - o - chlorophenyl - acetone (l) or benzil - monoxime (m); for the preparation of the compounds listed under (f) to (m), moreover, the 3-phenyl - 7 - hydrazino - coumarin was replaced with 3 - p - tolyl - 7 - hydrazino - coumarin.

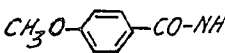
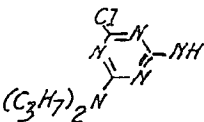
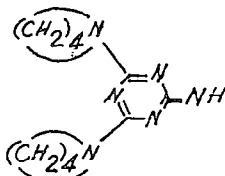
The compound listed under (n) was pre-

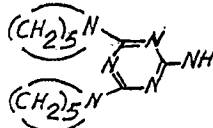
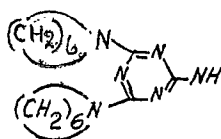
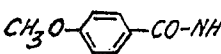
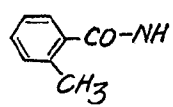
- pared in the following manner: 18 g (0.11 mole)  $\beta$ -aminocinnamic acid amide were dissolved in alcohol while heating and, after cooling, coupled in known manner at pH 5 and 5° to 10°C with the diazo compound of 23.7 g (0.1 mole) 3 - phenyl - 7 - amino-coumarin. The precipitated azo compound was filtered off with suction and stirred into 600 ml glycol monomethyl ether. After the addition of a solution of 40 g of crystalline copper (II) chloride in 200 ml of aqueous ammonia, the mixture was heated on a water bath while stirring and stirring on the water bath was continued for 4 hours to convert the copper complex formed. When no more complex copper compound could be detected, the mixture was poured into 2.5 litres of water, the resultant precipitate was filtered off with suction and recrystallised from dimethyl formamide, whereby the 3 - phenyl - 7 - [4-phenyl - 5 - carbonamido - v - triazolyl - (2)]-coumarin was obtained in the form of slightly

yellow crystals. The compound listed under (o) was prepared in an analogous manner by replacing the  $\beta$ -aminocinnamic acid amide with  $\beta$ -amino-crotonic acid ethyl ester, and the compounds listed under (p) and (q) were prepared by also replacing the 3 - phenyl - 7 - amino - coumarin with 3 - p - tolyl - 7 - amino - coumarin.

#### EXAMPLE 2

A fabric of polyester fibres is introduced in a liquor ratio of 1:40 into a bath containing, per litre, 1.5 g sodium oleyl-sulphate, 0.75 g formic acid and 0.1 g of one of the 7 - v - triazolyl - (2) - coumarin compounds of formula (I) listed in the Table below under (a) to (p) as brightening agent. The bath is heated to boiling temperature within 30 minutes and kept at boiling temperature for about 45 minutes, while the fabric is moderately moved about. The fabric is subsequently rinsed and dried. It exhibits an excellent neutral brightening effect.

7-v-Triazolyl-(2)-Coumarin compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Melting point °C.
a	H	CH <sub>3</sub> CO—NH	H	H	H	268—270°
b	H	C <sub>2</sub> H <sub>5</sub> CO—NH	H	H	H	228—230°
c	H	CH <sub>3</sub> —(CH <sub>2</sub> ) <sub>2</sub> —CO—NH	H	H	H	216—218°
d	H	(CH <sub>3</sub> ) <sub>2</sub> CH—CH <sub>2</sub> —CO—NH	H	H	H	220—221°
e	H	C <sub>2</sub> H <sub>5</sub> O—CH <sub>2</sub> —CO—NH	H	H	H	162—163°
f	H		H	H	H	255,5—256,5°
g	H		H	H	H	233—234°
h	H		H	H	H	231—233°

7-v-Triazolyl-(2)-Coumarin compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Melting point °C.
i	H		H	H	H	253—254°
k	H		H	H	H	205—206°
l	H	CH <sub>3</sub> CO—NH	H	CH <sub>3</sub>	H	257—258°
m	H	(CH <sub>3</sub> ) <sub>3</sub> C—CO—NH	H	CH <sub>3</sub>	H	243—244°
n	H	C <sub>2</sub> H <sub>5</sub> O—CH <sub>2</sub> —CO—NH	H	CH <sub>3</sub>	H	185—186,5°
o	H		H	CH <sub>3</sub>	H	252°
p	H		H	CH <sub>3</sub>	H	256—257°

The 7 - v - triazolyl - (2) - coumarin compounds listed in the Table under (a) to (k) were prepared as follows:

- 5 The diazo compound of 23.7 g. (0.1 mole) 3 - phenyl - 7 - amino - coumarin was coupled in known manner at 5 to 10°C and pH 5 with 11.5 g (0.11 mole) nitroacetaldoxime. The precipitated azo compound was filtered off with suction and, after drying, introduced into 350 ml acetic anhydride. The mixture was subsequently heated under reflux with stirring for 4 hours and then cooled. The precipitated nitro-triazole compound was filtered off with suction, washed with glacial acetic acid and recrystallised from dimethyl formamide. The 3 - phenyl - 7 - [4 - nitro - v - triazolyl - (2)] - coumarin of melting point 274°C so obtained was suspended at 50°C in dimethyl formamide and, after the addition of 10 g Raney nickel, hydrogenated at 50°C and under a hydrogen pressure of 50 at. When the absorption of hydrogen was completed, the solution was filtered off from the catalyst and the sol-

vent distilled off. The resultant 3 - phenyl - 7 - [4 - amino - v - triazolyl - (2)] - coumarin had a melting point of 231 to 232°C after recrystallisation from the methyl ether of ethylene glycol. The 3 - phenyl - 7 - [4 - amino - v - triazolyl - (2)] - coumarin was subsequently reacted with acetyl chloride (a), propionyl chloride (b), n-butyryl chloride (c), isovaleryl chloride (d), ethoxy-acetyl chloride (e), p-anisoyl chloride (f) or 2 - dipropylamino-4,6 - dichloro - 1,3,5 - triazine (g) or condensed first with cyanuric chloride and then with pyrrolidine (h), piperidine (i) or hexamethylene-imine (k).

The 7 - v - triazolyl - (2) - coumarin compounds listed under (l) to (p) were prepared in an analogous manner. The diazo compound of 3 - p - tolyl - 7 - amino - coumarin was coupled with nitroacetal-doxime, the resultant azo compound was converted with acetic anhydride into 3 - p - tolyl - 7 - [4 - nitro - v - triazolyl - (2)] - coumarin of melting point 261°C and this nitro compound was then

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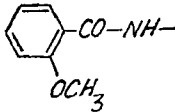

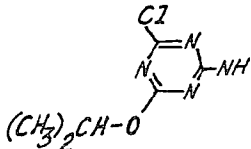
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- hydrogenated, after the addition of Raney nickel, in the manner described above to form 3 - p - tolyl - 7 - [4 - amino - v - triazolyl - (2)] - coumarin of melting point 236°C. The 3 - p - tolyl - 7 - [4 - amino - v - triazolyl - (2)] - coumarin so obtained was subsequently reacted with acetyl chloride (l), pivaloyl chloride (m), ethoxyacetyl chloride (n), p-anisoyl chloride (o) or o-toluy chloride (p).

## EXAMPLE 3

A fabric of cellulose acetate fibres is moved about in a liquor ratio of 1:40 and at 60°C for 45 minutes in an aqueous bath containing, per litre, 1 g sodium oleyl-sulphate, 0.75 g formic acid and 0.1 g of one of the 7 - v - triazolyl - (2) - coumarin compounds of formula (I) listed in the Table below as brightening agent. The fabric is subsequently rinsed and dried. After this treatment, the material is excellently brightened.

7-v-Triazolyl-(2)-coumarin compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Melting point °C.
(a)	H	C <sub>2</sub> H <sub>5</sub> O—CO—NH	H	CH <sub>3</sub>	H	250° (decomp.)
(b)	H		H	H	H	248—250°
(c)	H		H	CH <sub>3</sub>	H	267—268°
(d)	H		H	CH <sub>3</sub>	H	265° (decomp.)

- These 7 - v - triazolyl - (2) - coumarin compounds were obtained by reacting the 3-phenyl- or 3 - p - tolyl - 7 - [4 - amino - v - triazolyl - (2)] - coumarin described in Example 2 with chloroformic acid ethyl ester (a), 2 - methoxy - benzoyl chloride (b),  $\gamma$ -butyrolactone (c) or 2 - isopropoxy - 4,6 - dichloro - 1,3,5 - triazine (d).
- Good results are also obtained, when the 7 - v - triazolyl - (2) - coumarin compounds listed in the present Example under (a) to (d) are replaced with the compounds listed in Example 1 under (a), (c) and (f) and in Example 2 under (a), (e), (l) and (n).

## EXAMPLE 4

A fabric of polyester fibres is padded with

an aqueous liquor containing, per litre, 1 g of a commercial dispersing agent based on fatty alcohol polyglycol ethers, 1 g of a commercial wetting agent based on alkylnaphthalene sulphonic acids, 4 g of a commercial thickening agent based on sodium alginate and a solution of 1 g of one of the 7 - v - triazolyl - (2) - coumarin compounds of formula (I), in 20 g triethanol-amine which are listed in the Table of Example 1 under (a) to (q) or in the Table below under (a) to (o) as brightening agents. The fabric is squeezed to a weight increase of 100%, then dried, heated to 190°C for 1 minute and washed with hot water. Compared with the untreated material, the fabric thus treated exhibits a strong clear brightening effect of good fastness to light.

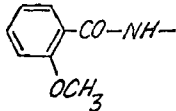
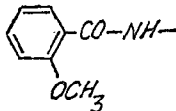
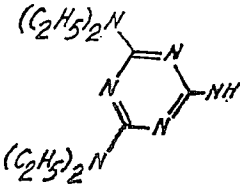
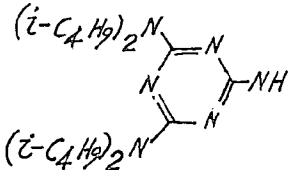
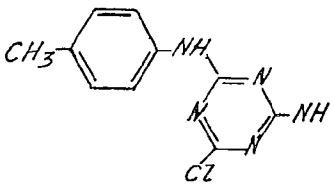
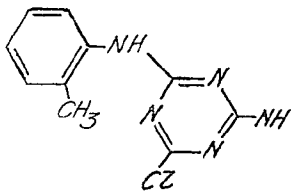
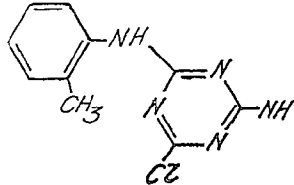
7-v-Triazolyl-(2)-coumarin compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Melting point °C.
a	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	H	H	H	116—118°
b	H	p—CH <sub>3</sub> —C <sub>6</sub> H <sub>4</sub>	H	H	H	291,5—293°
c	H	2,4—(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	H	245—247°
d	H	p—CH <sub>3</sub> O—C <sub>6</sub> H <sub>4</sub>	H	H	H	241—242°
e	CH <sub>3</sub>	o—CH <sub>3</sub> O—C <sub>6</sub> H <sub>4</sub>	H	H	H	176,5—177°
f	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	H	H	176—177,5°
g	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>	H	163—164°
h	H	p—CH <sub>3</sub> —C <sub>6</sub> H <sub>4</sub>	H	CH <sub>3</sub>	H	271—271,5°
i	H	2,4—(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	CH <sub>3</sub>	H	212,5—213°
k	CH <sub>3</sub>	o—CH <sub>3</sub> O—C <sub>6</sub> H <sub>4</sub>	H	CH <sub>3</sub>	H	174—175°
l	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	H	Cl	H	201—202°
m	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	OC <sub>4</sub> H <sub>9</sub>	H	153,5—154,5°
n	C <sub>6</sub> H <sub>5</sub>	COOC <sub>2</sub> H <sub>5</sub>	H	H	H	193—193,5°
o	C <sub>6</sub> H <sub>5</sub>	COOC <sub>2</sub> H <sub>5</sub>	H	CH <sub>3</sub>	H	198—199°

5 The 7 - v - triazolyl - (2) - coumarin compounds listed in the above Table under (a) to (m) were prepared in a manner analogous to the preparation of the 7 - v - triazolyl - (2) - coumarin compound in the Table of Example 1 under (a). For this purpose instead of diacetyl monoxime, 4-methyl - 3 - oximino-pentanone - 2 (a;g;l), p - methyl - oximino-acetophenone (b;h), 2,4 - dimethyl - oximino-acetophenone (c;i), p - methoxy - oximino-acetophenone (d), 1 - oximino - 1 - o - methoxyphenyl - acetone (e;k), oximino - valero-phenone (f) or oximino - propiophenone (m) were used; furthermore for the preparation of the compounds listed under (g) to (k) 3-p - tolyl - 7 - hydrazino - coumarin and for the preparation of the compounds listed under (l) and (m) 3 - p - chloro - phenyl - 7 - hydrazino - coumarin and 3 - p - n - butoxy-phenyl - 7 - hydrazino - coumarin respectively were used instead of 3 - phenyl - 7 - hydrazino - coumarin.

25 The 7 - v - triazolyl - (2) - coumarin compounds listed in the above Table under (n) and (o) were prepared in a manner analogous to the preparation of the 7 - v - triazolyl - (2) - coumarin compound listed in the Table of Example 1 under (n). For this purpose  $\beta$ -aminocinnamic acid ethyl ester was used instead of  $\beta$ -aminocinnamic acid amide and furthermore for the preparation of the 7 - v - triazolyl - (2) - coumarin compound listed under (o) 3 - p - tolyl - 7 - aminocoumarin was used instead of 3 - phenyl - 7 - amino- 35 coumarin.

#### EXAMPLE 5

1 Gram of one of the 7 - v - triazolyl - (2)-coumarin compounds of formula (I) listed in the following Table is incorporated as 40 brightening agent into 1000 g of an opaque soft polyvinyl chloride. The material is then excellently brightened and exhibits a neutral white shade.

7-v-Triazolyl (2)-coumarin compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Melting point °C.
a	H		H	H	H	248—250°
b	H		H	CH <sub>3</sub>	H	247—248,5°
c	H		H	CH <sub>3</sub>	H	218—220°
d	H		H	H	H	197—198°
e	H		H	CH <sub>3</sub>	H	287—289°
f	H		H	H	H	256—257° (decomp.)
g	H		H	CH <sub>3</sub>	H	255—256° (decomp.)



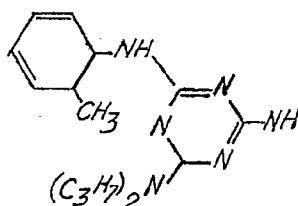
7-v-Triazolyl  
(2)-coumarin  
compound

R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>R<sub>5</sub>

Melting point  
°C.

h

H



H

H

H

215—216°

These 7 - v - triazolyl - (2) - coumarin compounds were obtained by reacting the 3-phenyl- or 3 - p - tolyl - 7 - [4 - amino - v - triazolyl - (2)] - coumarin described in Example 2 with o-anisoyl chloride (a;b), with cyanuric chloride and diethylamine or diisobutylamine (c;d), with 2 - p - toluidino - 4,6-dichloro - 1,3,5 - triazine (e), with 2 - o - toluidino - 4,6 - dichloro - 1,3,5 - triazine (f;g) and with 2 - o - toluidino - 4,6 - dichloro - 1,3,5 - triazine and dipropylamine (h).

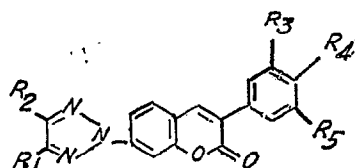
Good results are also obtained, when the 7 - v - triazolyl - (2) - coumarin compounds listed in the present Example under (a) to (h) are replaced with the compounds listed in Example 1 under (c), (e), (h), (l) and (m) and in Example 4 under (d), (e), (f), (i), (k), (l), (n) and (o).

#### EXAMPLE 6

1 Gram of one of the 7 - v - triazolyl - (2)-coumarin compounds listed in Example 1 under (c), (e), (h), (l) and (m), in Example 2 under (a), (e), and (l), in Example 4 under (d), (e), (f), (i), (k), (l), (n) and (o) and in Example 5 under (a) is dissolved in 1000 g of a colourless lacquer of nitrocellulose or cellulose acetate. The lacquer is then thinly spread on a colourless bottom. After drying, the lacquer film is excellently brightened.

#### WHAT WE CLAIM IS:—

1. Blue - fluorescent 7 - v - triazolyl - (2)-coumarin compounds of the formula



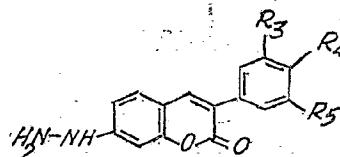
wherein R<sub>1</sub> is hydrogen or an unsubstituted

or substituted alkyl or aryl radical, R<sub>2</sub> is an unsubstituted or substituted alkyl or aryl radical, cyano, a carboxylic acid group, a carboxylic acid ester group, an unsubstituted or substituted carboxylic acid amide group or an acylated amino group, and R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub>, independently of one another, stand for hydrogen, halogen, alkyl radicals or alkoxy groups.

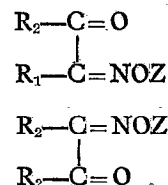
2. Compounds according to Claim 1, which are any of those hereinbefore specifically identified in Examples 1, 2, 3 and 5 and the Tables given in said Examples.

3. Compounds according to Claim 1, which are any of those specifically identified in Example 4 and the Table in said Example.

4. Process for producing compounds according to Claim 1, in the case where R<sub>2</sub> in the stated formula stands for an unsubstituted or substituted alkyl or aryl radical, by condensing a 7-hydrazino-coumarin derivative of the formula

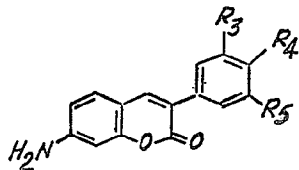


with an α-oximino-ketone of the formula

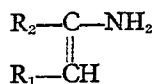


wherein Z stands for hydrogen or an acyl radical, and converting the resultant α-oximino-hydrazone into the 7 - v - triazolyl - (2) - coumarin compound with the elimination of HOZ.

5. Process for producing compounds according to Claim 1, in the case where in the formula stated  $R_2$  stands for cyano, a carboxyl group, a carboxylic acid ester group or an unsubstituted or substituted carboxylic acid amide group, by coupling a diazo compound of a 7-amino-coumarin derivative of the formula



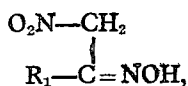
- 10 with an enamine of the formula



- 15 converting the resultant azo compound with an ammoniacal solution of a copper-(II) salt into the copper complex, and transforming the latter into the 7 - v - triazolyl - (2) - coumarin compound by heating.

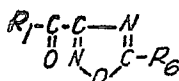
- 20 6. Process according to Claim 5, in which the compound obtained is hydrolysed to convert the carboxylic acid nitrile, ester or amide group into the carboxyl group.

- 25 7. Process for producing compounds according to Claim 1, in the case where in the stated formula  $R_2$  stands for an acylated amino group, by coupling a diazo compound of a 7-amino-coumarin derivative of the formula stated in Claim 5, with an  $\alpha$ -nitro-oxime of the formula

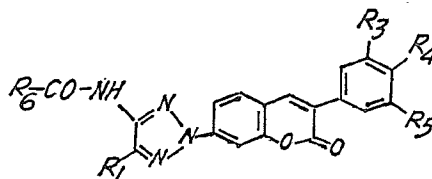


- 30 cyclising the resultant azo compound to form the corresponding 7 - [4 - nitro - triazolyl - (2)] - coumarin compound, reducing the nitro group to the amino group and converting the latter into the acylamino group.

- 35 8. Process for producing compounds according to Claim 1, in the case where in the stated formula  $R_2$  stands for an acylated amino group and  $R_1$  for an unsubstituted or substituted aryl radical, by condensing a 7-hydrazino-coumarin compound of the formula stated in Claim 4, with a 1,2,4-oxodiazole of the formula



wherein  $R_6$  stands for an alkyl or aryl radical, and rearranging the resultant hydrazone to form the 7 - v - triazolyl - (2) - coumarin compound of the formula



9. Process according to Claim 8, in which the acylamino group  $R_6-CO-NH$  is replaced with the acylamino group  $R_2$ .

10. Process for producing compounds according to Claim 1 carried out substantially as described in any one of the foregoing Examples 1, 2, 3 and 5, with reference to the Tables in said Examples.

11. Process for producing compounds according to Claim 1 carried out substantially as described in Example 4, with reference to the Table in said Example.

12. 7 - v - triazolyl - (2) - coumarin compounds when produced by a process according to any one of Claims 4—11.

13. Process for brightening fibre materials by applying thereto a brightening agent containing as the active ingredient a compound according to any of Claims 1—3 and 12.

14. Process according to Claim 13, in which the fibre material is of a polyester or polyvinylchloride.

15. Process for brightening articles or materials by incorporating into a substance from which the article or material is made, a brightening agent containing as the active ingredient a compound according to any one of Claims 1—3 and 12.

16. Process according to Claim 15, in which the article or material is a lacquer or varnish of a cellulose ester or nitrocellulose.

17. Process according to Claim 15, in which the article or material is a film, filament or any other shaped article.

18. Process for brightening articles or materials according to any of Claims 13—17 when performed substantially as described in any one of the foregoing Examples 1—3, 5 and 6.

19. Process for brightening articles or materials according to any of Claims 13—17 when performed substantially as described in Example 4.

20. Materials and articles when brightened by a process according to any one of Claims 13—19.

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